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13. ABSTRACT (Maximum 200 words)  The practical usefulness of carbon nanofibers depends on an economical process for creating the fibers. A process described in US Patent No 6,382,526 B1, referred to as the nanofiber by gas jet process, or briefly NGJ process was used to produce nanofibers from mesophase pitch, which were subsequently stabilized and carbonized to carbon fibers. The process produces nanofibers at such a high rate that it was necessary to move it out of a laboratory. Larger equipment and more space were acquired. Samples prepared were successfully stabilized and carbonized. Approximately 125 grams of carbonized nanofibers were sent to Dr. Heidi Schreuder-Gibson at the Army Natick Laboratory. As of this date the large scale machinery, consisting of an extruder, a large filter box, an air compressor, and an oven suitable for stabilizing the pitch fibers are together in one place, and ready to be put into operation. The NGJ apparatus continues to promise high productivity of carbon fibers with diameters around one micron, but further progress toward continuous high rate production was stalled by inadequate operating resources.					
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Final report "Nanofiber Production by Gas Jet Spinning Method (NGJ) for Chemical Protective Clothing"

## 1. Abstract

The practical usefulness of carbon nanofibers depends on an economical process for creating the fibers. A process described in US Patent No 6,382,526 B1, referred to as the nanofiber by gas jet process, or briefly NGJ process was used to produce nanofibers from mesophase pitch, which were subsequently stabilized and carbonized to carbon fibers. The process produces nanofibers at such a high rate that it was necessary to move it out of a laboratory. Larger equipment and more space were acquired. Samples prepared were successfully stabilized and carbonized. Approximately 125 grams of carbonized nanofibers were sent to Dr. Heidi Schreuder-Gibson at the Army Natick Laboratory. As of this date the large scale machinery, consisting of an extruder, a large filter box, an air compressor, and an oven suitable for stabilizing the pitch fibers are together in one place, and ready to be put into operation. The NGJ apparatus continues to promise high productivity of carbon fibers with diameters around one micron, but further progress toward continuous high rate production was stalled by inadequate operating resources.

## 2. Introduction

The production of carbon fibers with diameters in the range around 1 micron, from mesophase pitch was undertaken to incorporate the carbon nanofibers into a polymer matrix by the needle looming process. A longer-term goal is the preparation of highly absorptive carbon nanofibers for various applications in the design and construction of protective clothing.

The intent of this project was to scale up the production of carbon nanofibers produced from mesophase pitch by a gas jet spinning method called the NGJ process, which utilizes a patented nozzle design, and produced fibers at a rate much higher than the electrospinning processes also developed at the University of Akron. Figure 1 shows a drawing of the NGJ nozzle. A more detailed description of the nozzle is given in the following patent:

United States Patent No. US 6,382,526 B1, May 7, 2002

**"PROCESS AND APPARATUS FOR THE PRODUCTION OF NANOFIBERS"**

Inventors: Darrell H. Reneker, Iksoo Chun, Dale Ertley

Assignee: The University of Akron

U.S. Patent

May 7, 2002

Sheet 1 of 3

US 6,382,526 B1

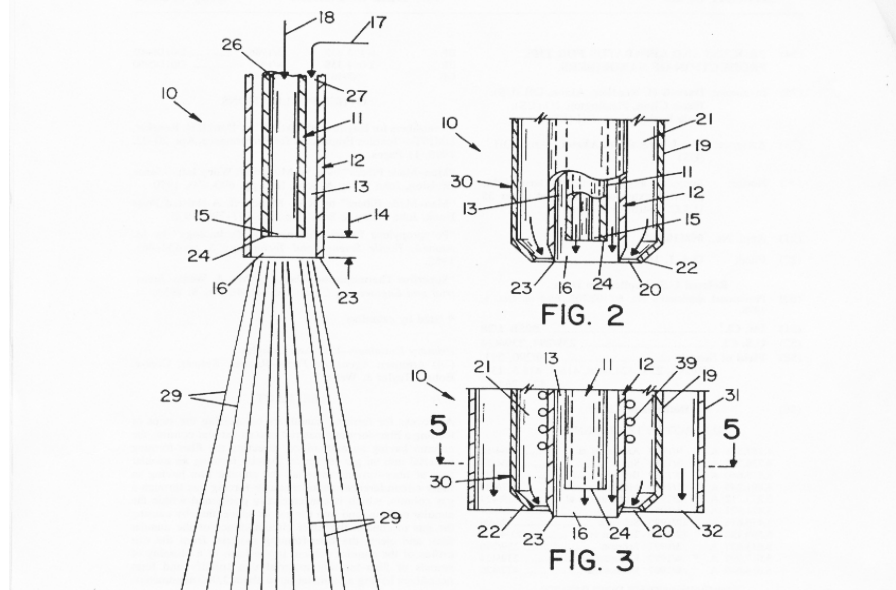


Figure 1 Diagram of nozzle for the NGJ process

The carbon fibers produced by using the NGJ process have length to diameter ratios that are reasonably high, and the length of individual fibers ranges from a few millimeters to a few centimeters. See Figures 2 and 3 below, which show fibers made using an early laboratory scale version of the apparatus. Carbon fibers with in this length range with diameters ranging upwards from a few hundred nanometers are not now available from a large scale process.

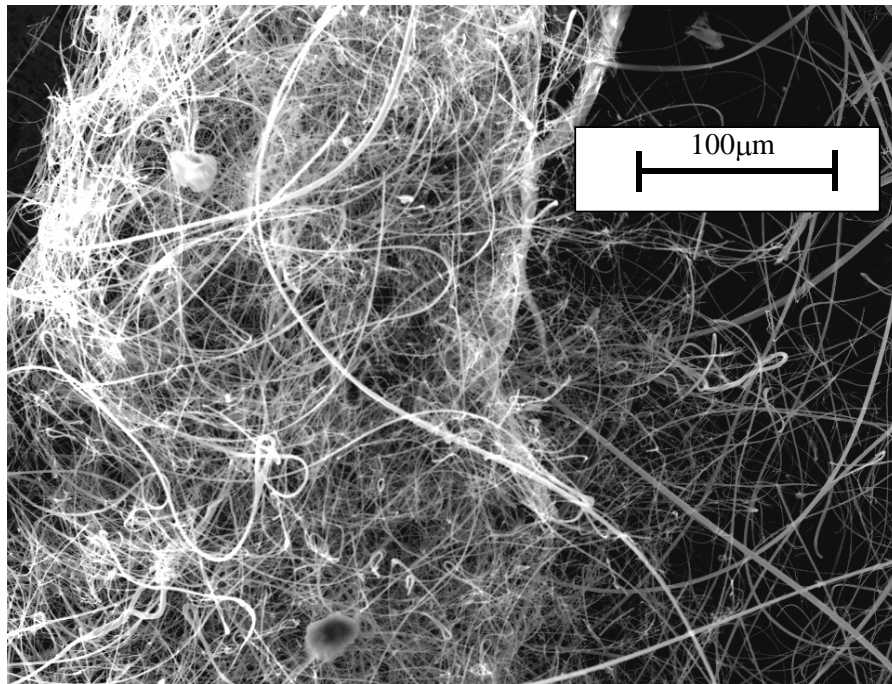


Figure 2 Carbon nanofibers made from mesophase pitch using the NGJ process.  
The bottom edge of the area shown is 5.5 mm across.

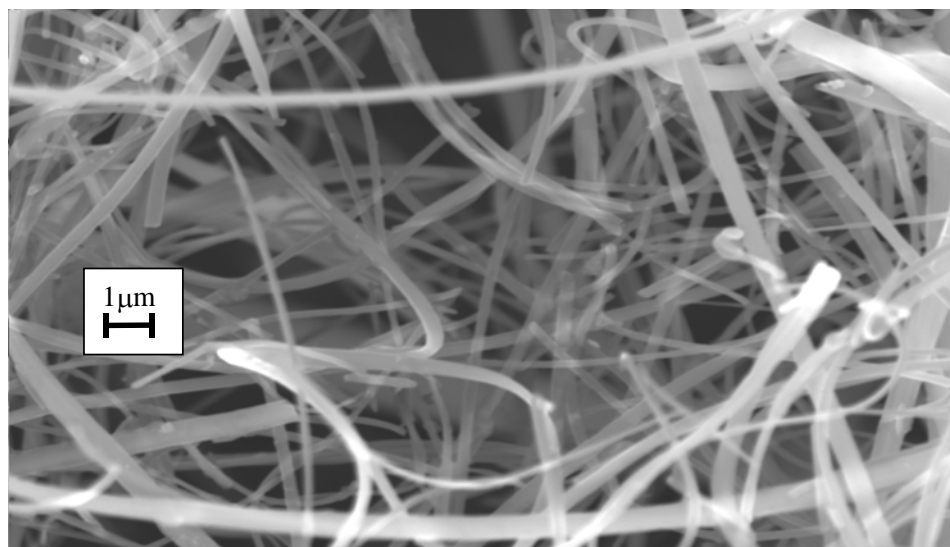


Figure 3. Area shown is from center of Figure 1. Most of the fibers have diameters of less than one micron. The bottom edge of the figure is 22 microns wide.

The NGJ process uses hot gas to make nanofibers from mesophase pitch.<sup>[1,2]</sup> The fibers are collected from the gas stream, stabilized by heating to 300 °C in air, and then carbonized by heating to around 1000 °C in an inert gas such as nitrogen. A typical sample of carbon fibers contains many nanofibers, along with larger diameter fibers. The larger fibers, with diameters of 1 to 10 microns, provide mechanical support for the smaller fibers. Figure 1 is a scanning electron micrograph that shows an area that is about one-half a millimeter across. Many of the larger fibers were seen to be over a millimeter long by observing them at lower magnification in the optical microscope. Figure 2 shows an area near the center of Figure 1 that is about 20 microns across. This area is filled with nanofibers with a distribution of diameters that is centered around 500 nanometers. This multitude of nanofibers contributes most of the surface area of such a collection of fibers. The longer fibers contribute strength to the network, which is desirable in some applications. The relative proportions of the pitch fibers with different diameters and lengths was seen to be affected by processing conditions at the nozzle, and this control will be exercised in the planned work.

Part of this batch of carbonized fibers was used to test a mechanical process called “needling”. The first results from the needling process indicate a need for larger samples in uniform sheets, perhaps with a polymeric binder, to hold the nanofibers in place during the early stage of the needling process. Dr. Seshadri S. Ramkumar, is developing the needling process at Texas Technical University in Lubbock, Texas.

### 3. Initial progress toward production of larger quantities of carbon fibers

The stabilization, carbonization, and characterization of carbon nanofibers produced from mesophase pitch by a gas jet spinning method called the NGJ process was undertaken. Our capacity for stabilization of the pitch nanofibers, by heat-treating in air at up to 300 °C, was increased by refurbishing a large oven. Access was arranged to use a suitably large controlled atmosphere high temperature oven for the carbonization process.

Synthesized Mesophase Pitch, ARHP was obtained from Mitsubishi Gas Chemical Company, Inc. This pitch has a somewhat higher softening point (271.8°C) than the ARA-24 pitch used in the earlier work (210 to 260°C).

Other specifications of the mesophase pitch are shown in the box below.

Specifications of ARHP from:  
Certificate of Analysis done on 9 Aug 1999  
At Mizuma factory by T Ojima, Head of Analytical  
Section  
Lot No. 9024

**ARHP:**

Features-Lower Volatile than ARMP  
Typical Applications- Continuous Graphite  
Fiber

**Physical Properties:**

Appearance- Black Pellet  
Bulk Density- 0.66 g/cc  
Specific Gravity- 1.23 @ 25°C  
Specific Heat- 0.65 cal/g °C  
Softening Point- 271.8°C  
Mesophase Content- 100%  
Hydrogen/Carbon (atom/atom)- 0.58~0.64  
Flash Point- >300°C  
Ash- <20ppm

**Solubility:**

Water Soluble- 0  
Benzene Soluble- 35~44  
Pyridine Insoluble- 40~50

The NJG (Nanofibers by Gas Jet) process was first set up in one of our regular laboratories in the Department of Polymer Science of the University of Akron. A small extruder fed molten pitch to an NGJ jet which was supplied with heated air for the operation of the gas jet. The extruder and the nozzle were provided with conventional band heaters and appropriate insulation to heat the extruder, transfer tubes, and the nozzle to temperatures at which the pitch is molten, but not caused to react by partial oxidation or to carbonize to a significant degree.

Improved nozzle construction and improvement in process machinery brought the process under better control. This apparatus was successful and was used to create many batches of pitch nanofibers some of which were stabilized and carbonized in laboratory scale ovens and furnaces. The pitch nanofibers were collected from the air jet used to produce them with a filter having an area of less than one square meter. The rate of production of pitch nanofibers was so high with the improved NJG system that the system could run for only a few minutes before the collection system was overloaded with nanofibers. At that point, the airstream carrying the fibers began to

flow out of the entrance to the filter box, releasing the nanofibers into the laboratory. This situation was intolerable for reasons including laboratory contamination, interference with other research projects, and possible health and safety issues.

The “Single run sample” was made under the conditions shown in the box below:

01-18-01 2<sup>nd</sup> Run

Nozzle: SVO3

14.5g of Fiber

T= 270° C - Extruder

620° C - Jacket

540° C - Under

520° C - Lip

P(center air) = 95psi

= 70, 50, 30

P(lip) = 40psi

The temperatures are at various places on the apparatus when the process was running well. The relation of these measurements to the actual temperature of the pitch is not known, but most likely the maximum temperature of the pitch was closer to the extruder temperature, with a short burst of heating immediately before the fibers formed. The most important air pressure (center air) was reduced as the run progressed to 30 psi in 20 psi steps. Fibers made at the various center air pressures are aggregated in “single run” The lip air pressure was held at 40 psi.

The good news was that we have a process which is very productive, and produced pitch nanofibers at an impressive rate. The bad news was that we did not have a collection system that could handle large quantities of fibrous material. Clearly, the solution to this dilemma was to create a collection system with a greater capacity. A larger filter box and a larger work area to transfer nanofibers from the collection box to the stabilization furnace and finally to the carbonization furnace were essential.

We acquired, as a gift from industry to the University of Akron, a large bag filter box with a system for momentarily reversing the air flow through the collection filters, so that the layer of pitch nanofibers that collected on the active surface of the multiple bag filters could be blown off the bags and collected at the bottom of the filter box. See Figure 4.



Figure 4. Filter box on truck shows the size of the box.



An air compressor and a large oven for the thermal stabilization treatment of the pitch nanofibers at up to 300 °C in air were obtained at no cost to this project.

All these things were moved into a University owned building which had previously been used as an automobile paint shop. This space housed the extruder, the large filter box, a large oven, and a large air compressor to run the NGJ process and provide air for the reverse pulse of air needed to clear the filter surfaces. See Figure 5. Although very little dust is generated during handling of the nanofibers, an inexpensive but effective temporary wall with airlocks and other means to prevent the scattering of fibers was constructed by a contractor used by our Safety Office to control airborne dust in construction areas.

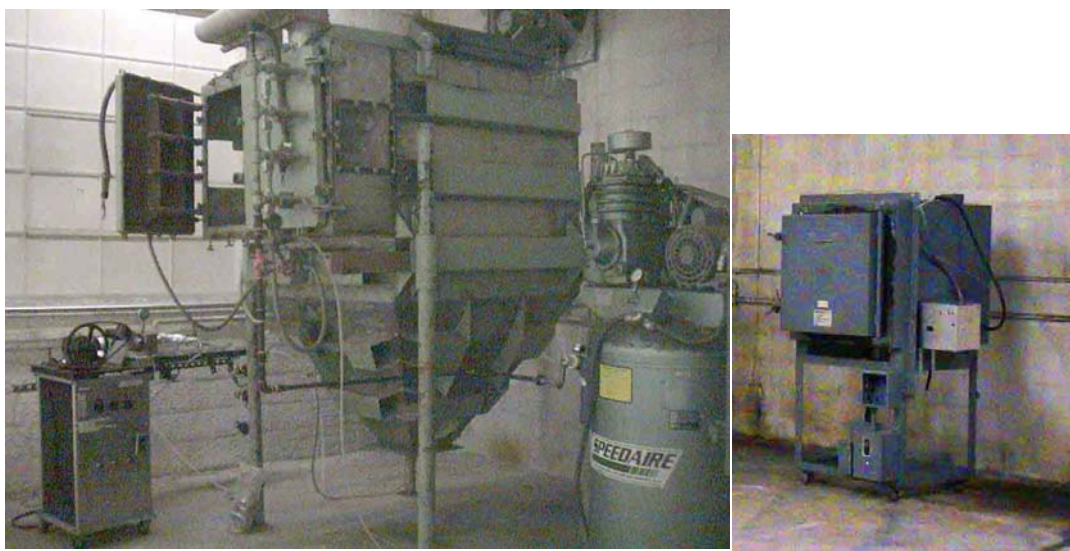


Figure 5 . Extruder at left, filter box center, air compressor, right.  
Stabilization furnace, at far right.

Financial support for people to operate this process, anticipated from various sources, was not forthcoming. Before this entire system could be put into operation, the funds for the project were exhausted. The NGJ apparatus and the stabilizing furnace are presently operational.

Attention was turned to stabilizing and carbonizing the nanofibers made in the laboratory scale apparatus. Rectangular stainless steel boxes, about 20 by 22 inches square and 6 inches deep were fabricated to fit into both the stabilization oven and into a commercial vacuum heat treating oven. This enables mesophase pitch fibers from the NGJ process to be collected with a minimum of handling, which is important because, before heat treatment, the pitch nanofibers are weak and brittle. High strength is achieved after the heat treatment in a vacuum, at which point the fibers can be handled in usual ways with no significant breakage.

Several batches of pitch nanofibers were combined in one of the steel boxes, and material from the best small scale run were placed in the other box. This material was successfully stabilized in one run of the stabilization furnace. The time temperature curve for this stabilization run is shown in Figure 6.

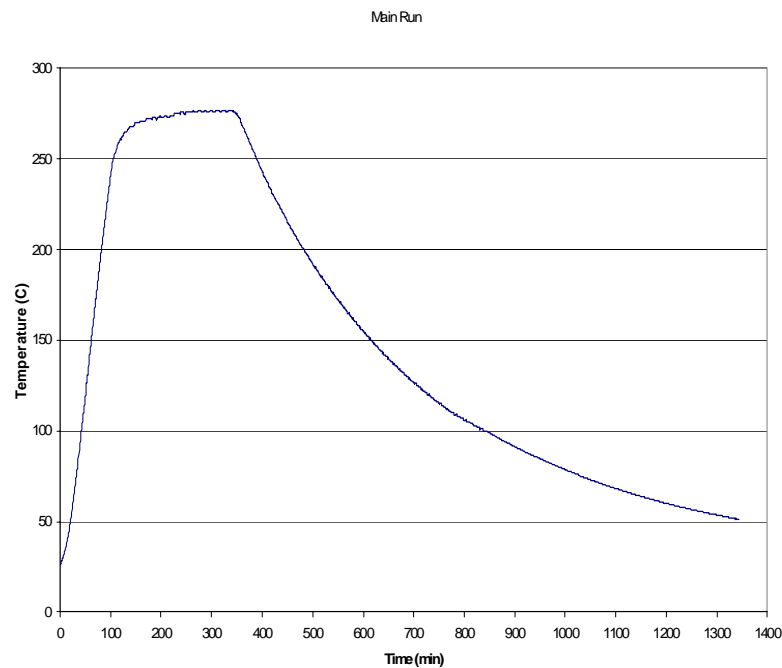


Figure 6 Temperature versus time, in minutes, for stabilization in air.

The “combined run sample” and the “best run sample” were then heat treated in a commercial vacuum furnace. See Figure 7 and Figure 8. The “combined run sample” includes pitch nanofibers made at various times, with varying morphology and varying operating parameters on the NGJ system. The diameters of the carbon nanofibers vary over a broad range. Some “shot”, (small balls of pitch, sometimes having a fiber tail) is present. Particularly, there are a number of relatively short carbon fibers in this sample.

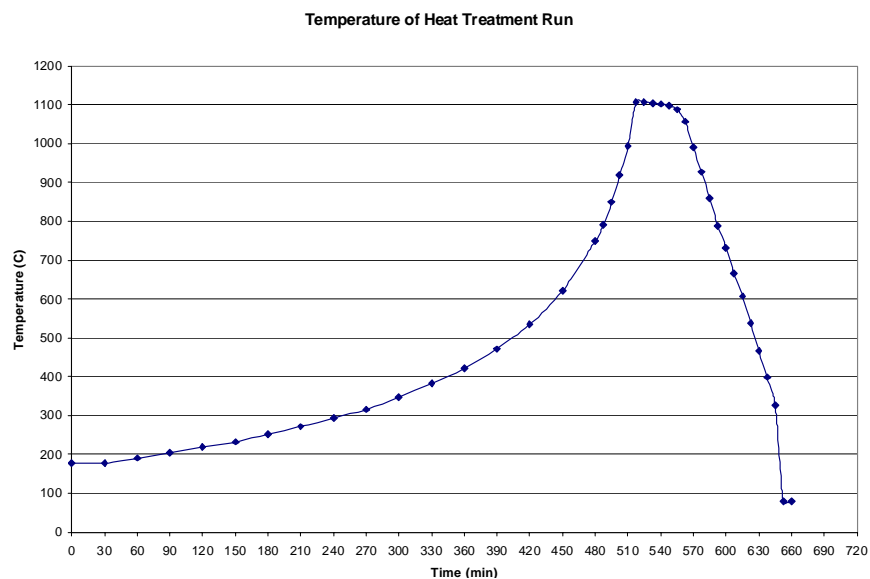


Figure 7. Temperature versus time for carbonization process.

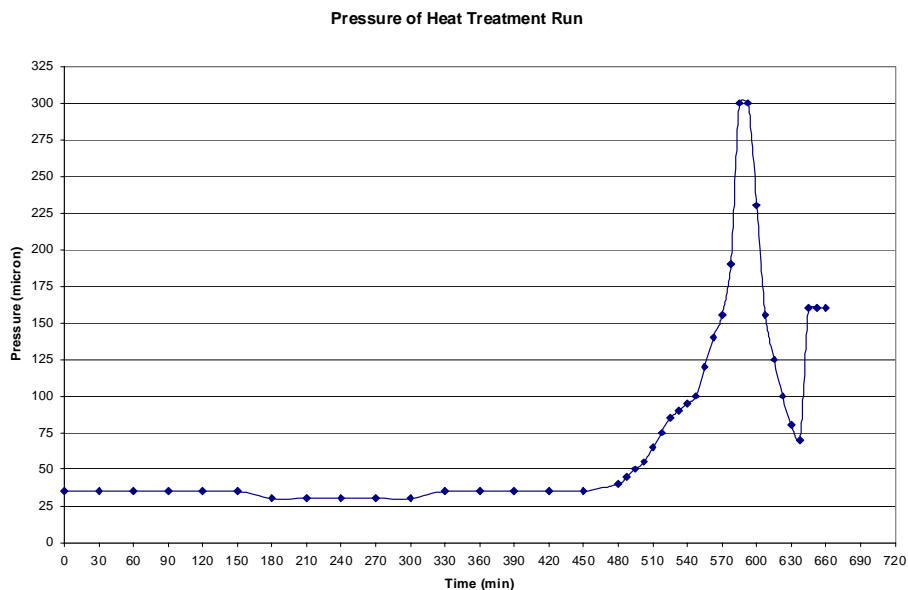


Figure 8 Pressure is vacuum furnace during carbonization of both the “Combined run sample” and the “Single Run Sample”

#### 4. Summary of material produced.

The resulting carbon nanofibers from the best run sample were characterized by scanning electron microscopy. It was found that gentle stirring of the stabilized nanofibers in boiling water produced a good dispersion for microscopic examination. Vigorous stirring with a magnetic stirrer of clusters of fibers from the high temperature heat treatment broke the fibers into short lengths. Figure 9 shows an optical micrograph of a large number of carbon fibers. The lengths varied from more than a millimeter to a few tenths of a millimeter. Scanning electron micrographs of the carbonized fibers also dispersed gently in boiling water are shown in Figure 10. The diameters of the fibers, shown in higher magnification scanning electron micrographs, of Figure 10 ranged from a few hundred nanometers to as large as 5 microns.



Figure 9. Optical micrograph from the “Single sample run”

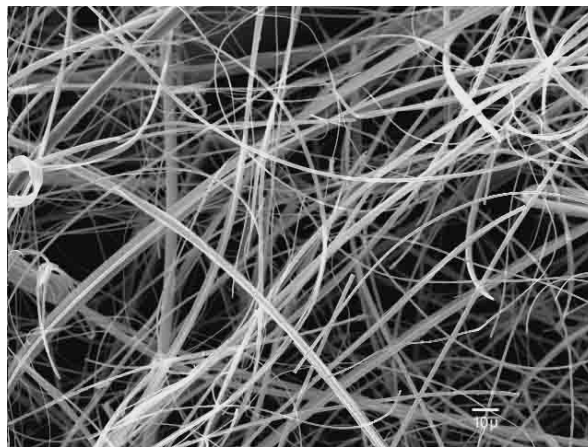
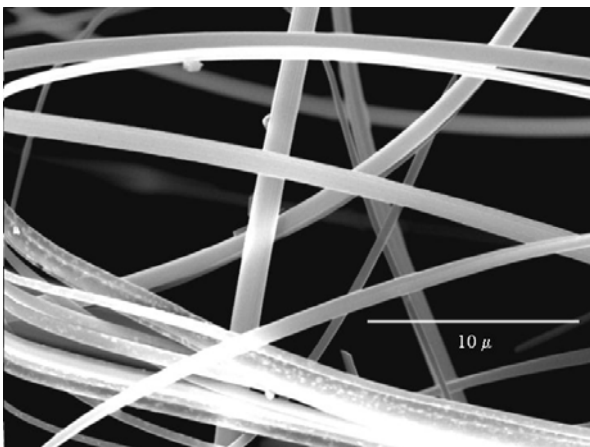


Figure 10 Representative fibers from the “Single sample run” shown at high magnification, on the left, and a larger field of view, on the right.

The samples that are being sent to Heidi Schreuder Gibson, at the Army Laboratory in Natick Massachusetts, who is the technical contact for this project, are summarized in the table below.

	Single run sample	Combined Run Sample
Electron Micrograph Fig. #	10	---
Total mass sent to Army	16.194g	105.495g
Stabilization Time (In air)	200 min	200 min
Stabilization Temperature	277°C	277°C
Carbonization Time (Vac.)	42 min	42 min
Carbonization Temperature	1107°C	1107°C
Micrograph	Figure 9	---

The observed heterogeneity in diameter is attributed partly to the fact that the process did not have time to stabilize before the process had to be stopped to clear the collection system. A significant fraction of the fibers were made while the process was starting and stopping.

Experiments to activate the carbon nanofibers to produce higher surface area per unit mass were planned, but not undertaken. The activation processes of interest include the incorporation of other elements into the nanofibers, and heat treatment in different gaseous atmospheres.

In a series of papers<sup>[3, 4, 5]</sup>, activated charcoal cloth was prepared by pretreatment of viscose rayon with transition metal oxo-complexes (Molybdenum, Vanadium and Tungsten), with Fe and Co chlorides, boron containing compounds, and phosphate compounds followed by carbonization in nitrogen and activation in carbon dioxide at 850°C. Surface areas per unit mass of the activated cellulose derived from BET measurements were in the range from 207 to 1412 m<sup>2</sup>g<sup>-1</sup>.

### Acknowledgements

Camden Ertley, Steven Roberts, Vesselin H. Velikov all contributed to this project.

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